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Gold nanoparticle wire and integrated wire array for electronic detection of chemical and biological molecules

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Nanoparticle wire and integrated nanoparticle wire array have been prepared through a green technique: discontinuous vertical evaporation-driven colloidal deposition. The conducting gold nanoparticle wire made by this technique shows ability for the sensitive electronic detection of chemical and biological molecules due to its high surface to volume ratio. Furthermore, we also demonstrate a potential usage of integrated gold nanoparticle wire array for the localized detection. *Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License*. [doi:10.1063/1.3568815]

Nanotechnology has the potential to revolutionize the future. Research on nanoscale particles has been an extremely active area with promises of advanced materials.[1–7] Prior to integrating various functional nanoparticles into electronic and photonic devices and catalytic reactions, the development of techniques for the precise control of the spatial arrangement of the building blocks on the nanometer and sub-nanometer levels is crucial to the design and fabrication of advanced devices.[8–11] The assembly of colloidal nanoparticles into functional structures is an exiting area of research for potential nanotechnology applications.[12] Recently, the assembly of particles of nanometer size has attracted significant interest for applications such as sensors and nanocoating.[13,14] There are many research activities devoted to the development of nanoparticle structure fabrication methods and functional properties, such as chemical deposition method and dielectrophoresis.[15,16]

Most recently, substantial amount of techniques with advantages over others with respect to simplicity, scale, resolution, and cost, have been developed to make one-dimensional (1D) nanoparticle structures.[17–24] In this paper, conducting gold nanoparticle wire and integrated wire array made by discontinuous Vertical Evaporation-driven Colloidal Deposition (VECD) are used for chemical and biological detections. Due to the high surface to volume ratio, these porous nanoparticle structures show a potential usage for the highly sensitive electric detection, as well as the localized detection.

As reviewed by Dahl and coworkers, VECD technique itself has been regarded as a greener effort, which reduces or eliminates the use or generation of hazardous substances,[3] for preparing various nanoparticle structures at room temperature and atmospheric pressure.[21,25] The deposition process of VECD is shown in Fig. 1(a). The nanoparticles close to solid-liquid-gas interface region, called meniscus, grow on substrate under the influence of interface force when partially immerged substrate moves relatively to suspension surface. When the deposition is continuous, a nanoparticle thin film is formed as a two-dimensional (2D) nanoparticle structure. The experimental and theoretical discussions of continuous deposition for nanoparticle films have been reported in previous papers.[25–27] On the application side, the gold nanoparticle thin film made by VECD has been used as a good platform for the soft laser desorption/ionization mass spectrometry.[28]

While uninterrupted deposition results in a continuous nanoparticle thin film, deposition followed by rapid removal of a small quantity of the suspension leads to the formation of 1D nanoparticle

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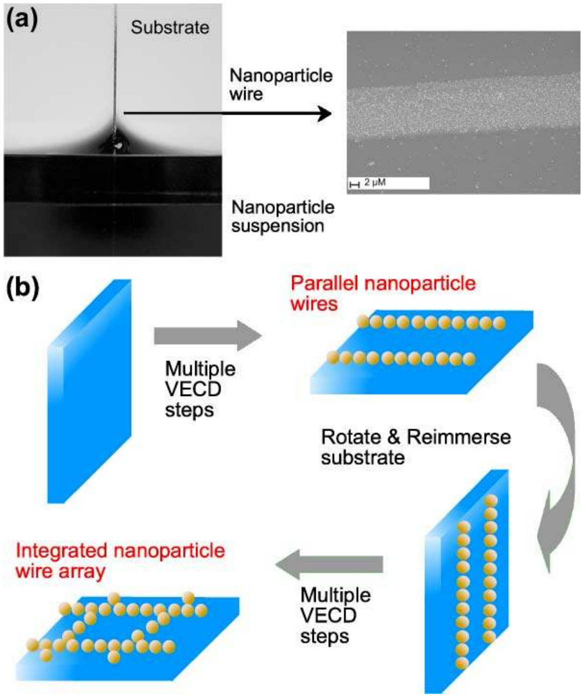

FIG. 1. (a) An optical image of the meniscus region of the vertical evaporation-driven colloidal deposition (VECD). When the deposition is uninterrupted, a continuous nanoparticle thin film is formed as a 2D nanoparticle structure. When the deposition is interrupted by rapid removal of a small quantity of the suspension, a nanoparticle wire is formed as a 1D nanoparticle structure. The inset is a scanning electron microscopy (SEM, LEO 1460VP) image of a gold nanoparticle wire made by discontinuous VECD through a 2-minute deposition. (b) Schematics of the preparation process of integrated nanoparticle wire arrays through a multi-round discontinuous VECD. Parallel nanoparticle wires and integrated nanoparticle wire arrays are formed after the first and the second deposition step, respectively.

wire structure.[21] The wire is formed along their width direction, and the width is determined by the evaporation rate and the deposition time: speeds of hundred nanometers per second and times of several seconds to minutes.[21] The repetition of this process forms parallel nanoparticle wires on the substrate. After being deposited a layer of parallel wires, the substrate is removed from suspension, rotated by an angle, and reimmersed. Following a second round of discontinuous VECD, another layer of parallel wires is deposited to form an integrated nanoparticle wire array (Fig. 1(b)). Parallel gold nanoparticle wires were obtained after deposition of the first layer (Fig. 2(a)). Subsequently, two different 7 × 7 integrated gold nanoparticle wire arrays were made by the second layer deposition with 90° (Fig. 2(b)) and 45° rotations (Fig. 2(c)). The multi-round deposition strategy can be used for double-component nanoparticles wire arrays by switching to a different nanoparticle suspension during the second layer deposition (Fig. 2(d) and 2(e)).

Conducting gold nanoparticle wires with ohmic behavior were produced through discontinuous VECD by using 12 ± 1 nm gold nanoparticles in weight concentrations of 0.02%. Various deposition times result the wire width ranging from several to hundred micrometers with a 100 nm thickness.[21] Since the conductance of porous gold nanoparticle wires made by discontinuous VECD is influenced by the local environment,[21,25] these conducting nanoparticle wires are promising to use in sensitive electric detections for chemical and biological objects because of the high surface to volume ratio. To test this, similar gold nanoparticle wires were painted with gold electrodes by the electron beam evaporator (Teme scasl BJD1800), and then measured by a semiconductor parameter analyzer (HP 4155A) or a lock-in amplifier (Signal Recovery 7265) through a probe station system. The resistance of gold nanoparticle wires used in our study was typically ranging from 100 to 500 Ω, significantly larger than the contact resistance measured as several ohms by putting two probes on one gold electrode, and hence our observations are mainly contributed from gold nanoparticle wires.

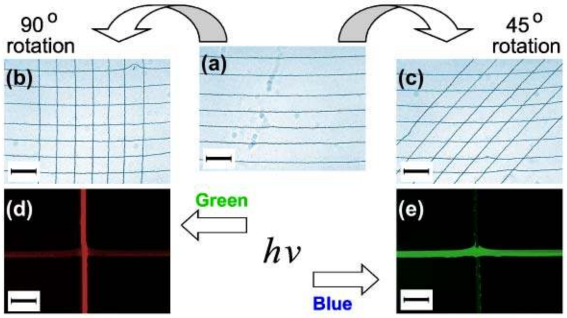

FIG. 2. Optical images of parallel gold nanoparticle wires (a) and integrated gold nanoparticle wire arrays made by the multi-round discontinuous VECD with 90° (b) and 45° rotations (c). The 10-second deposition was used for all wires. Fluorescent images of a 1 × 1 polymer nanosphere array by different excitation lights, green (d) and blue (e). 100 nm red and green fluorescent nanospheres were used in a 2-minute deposition. Scale bars are 100 μm in all images.

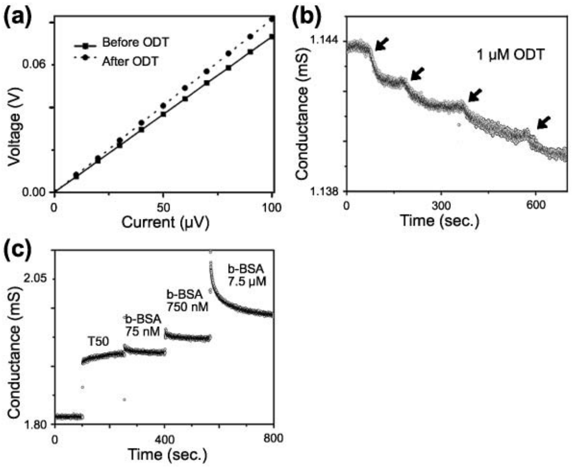

FIG. 3. (a) The current-voltage curves for a 5-minute deposition gold nanoparticle wire (0.5 mm long) before (solid line) and after (dot line) exploring to 5 μL, 1 mM ODT/ethanol solution. (b) The conductance changes of a 5-minute deposition gold nanoparticle wire through continuously adding 5 μL, 1 μM ODT/ethanol solution. (c) The conductance changes of a 10-minute deposition gold nanoparticle wire after sequentially adding biotin Bovine Serum Albumin (b-BSA) protein of concentrations of 75 nM, 750 nM, and 7.5 μM in T50 buffer. Current-voltage (I-V) responses were taken by a semiconductor parameter analyzer (HP 4155A) with a probe station system. The conductance measurement was performed by a lock-in amplifier (Signal Recovery 7265) with a probe station system.

The conductance of gold can be influenced by the thiol environment because of a significant decrease of 5d electron.[29] As shown in Fig. 3(a), after putting 1 mM solution of octadecanethiol (ODT, Sigma-Aldrich) dissolved in ethanol on a 0.5 mm-long gold nanoparticle wire with a 5-minute deposition, the resistance increased by ∼11.3%. Because of the high surface to volume ratio, the resistance increase of our gold nanoparticle wire is about ten times larger than what obtained on thiol modified gold thin film.[30] Furthermore, this increase is about 3 times larger than what discovered on the porous gold nanowire made by an *in situ* etching with the same ODT concentration.[31] As shown in Fig. 3(b), 0.1% conductance decrease was observed while adding 5 μL, 1 μM ODT/ethanol (5×10^{-12} mol ODT), which gives a 2.5-time higher sensitivity over the porous gold nanowire.[31]

Besides chemical molecules, large biological objects such as protein and virus can influence the electric behavior of nanowires.[32,33] In order to test our gold nanoparticle wires, different concentrations of biotin Bovine Serum Albumin (b-BSA) protein in the T50 buffer (10 mM Tris, 50 mM NaCl, pH 8.0) were applied on a gold nanoparticle wire made by a 10-minute deposition. As shown in Fig. 3(c), after adding T50 buffer as a background check, 75 nM, 750 nM, and 7.5 μM

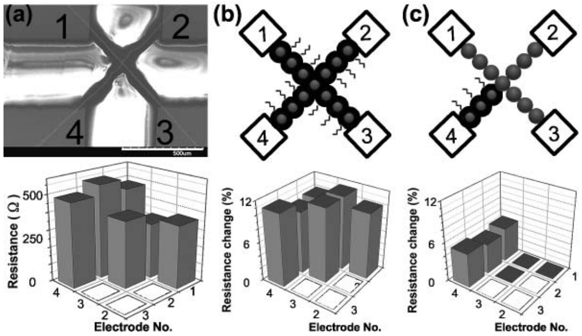

FIG. 4. (a) The scanning electron microscopy (SEM) micrograph and the resistance matrix of a 1 × 1 gold nanoparticle array by a 5-minute deposition for each wire. The numbers in the SEM image are used to label the electrodes relating to the resistance matrix. Scale bar is 500 μm in SEM image. (b) The resistance change of a 1 × 1 gold nanoparticle array by putting 5 μL, 1 mM ODT/ethanol solution on all wires. The average increase of resistance is 10.5%. (c) The resistance change of a 1 × 1 gold nanoparticle array by putting 5 μL, 1 mM ODT/ethanol solution only on the fourth branch which is roughly from the junction to the No.4 electrode. The average increase of resistance is 5.0%. 5-minute deposition was used for all wires.

b-BSA were added sequentially. We started to catch a conductance change after 750 nM b-BSA, and another change with a higher magnitude was obtained after 7.5 μM b-BSA. This experiment demonstrates a capability of using gold nanoparticle wires to detect b-BSA with concentration low down to several hundred nanomolars. Since 75 nM b-BSA did not induce a conductance change, as a control group, the influence from the buffer and the volume change can be ignored in all experiments.

Conducting gold nanoparticle wire arrays can also be made through the multi-step discontinuous VECD at ambient conditions. As shown in Fig. 4(a), a 1 × 1 conducting array formed by a 5-minute deposition was successfully obtained on glass substrates. The typical length of each wire ranged from 0.4 to 0.7 mm. As indicated by resistance matrices in Fig. 4(a), since $R_{13} + R_{24}$ is approximately equal to $R_{12} + R_{34}$ or $R_{14} + R_{23}$, the resistance across wire junctions can be ignored. The advantage of employing an array over single nanoparticle wire is the potential for the localized detection. To demonstrate this, two 1 × 1 gold nanoparticle arrays, similar to the array shown in Fig. 4(a), with a 5-minute deposition for each wire were used. As shown in Fig. 4(b), after putting 5 μL, 1 mM ODT/ethanol solution on all wires of one array, the resistance between any two electrodes increased by 10.5% in average. When we put 5 μL, 1 mM ODT/ethanol solution only on the 4th branch of another array (from the junction to the No.4 electrode), as shown in Fig. 4(c), the resistance between any two electrodes only changed when it's related to the No.4 electrode, and with a smaller increase of ~5%. During the second experiment, all other three branches were covered with vinyl electrical tape (3M) and epoxy glue (Devcon). Thus, beside the detection ability, arrays also tell the specific location relating to the electrode.

Nanoparticle wires were successfully prepared by a green method: discontinuous vertical evaporation-driven colloidal deposition, which is shown to be a simple and versatile method for wide usage. Conducting gold nanoparticle wires made through this method are used for the electric detection of chemical and biological molecules. Various concentrations of ODT and b-BSA molecules are tested in this paper. Due to the high surface to volume ratio, this nanoporous structure showed a potential for sensitive electric detections. Furthermore, integrated nanoparticle wire arrays are prepared by a multi-round discontinuous VECD technique for both metallic and nonmetallic nanoparticles. The conducting integrated nanoparticle wire arrays also promised a nice application in localized electric detections.

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